

Early Proterozoic (2.04 Ga) phosphorites of Pechenga Greenstone Belt and their origin

Alexei Yu. Rozanov^a, Marina M. Astafieva^{*a}, Richard B. Hoover^b

^aPaleontological Institute of Russian Academy of Sciences, 117997 Profsoyusnaya 123,
Moscow, Russia

^bNASA/National Space Science and Technology Center, 320 Sparkman Dr.,
Huntsville, Alabama, 35802, USA

ABSTRACT

No principal differences have been found between microfossils described from Cambrian and Phanerozoic and the 2000 Ma phosphorites. Numerous samples revealed diverse microbial microstructures interpreted as cyanobacterial mats consisting of filamentous (1-3 μm in diameter, 20 μm in length), coccoidal (0.8-1.0 μm) and ellipsoidal or rod-shaped microfossils (0.8 μm in diameter, around 2 μm in length) which morphologically resemble modern *Microcoleus* and *Siphonophycus*, *Thiocapsa*, and *Rhabdoderma*, respectively, reported from alkaline or saline environments. The sequence of the early Palaeoproterozoic events which point to a significant oxidation of the hydrosphere, including the formation of phosphorites and changes in the phosphorous cycle, mimics the sequence which was repeated at the Neoproterozoic-Cambrian transition, implying that oxidation of the terrestrial atmosphere-hydrosphere system experienced an irregular cyclic development.

Keywords: Lower Proterozoic, phosphorites, bacteria, cyanobacteria, cocci, filaments, framboids, Eukaryotes

Some biomorphic structures found in carbonaceous meteorites are practically indistinguishable from biomorphic structures encountered in Earth rocks, such as phosphorites. That is why one of the most ancient (Early Proterozoic) phosphorites from Pechenga Greenstone belt was chosen for the investigation of fossil bacterial remains.

In the history of the development of the Earth, a few stages of phosphoritogenesis can be distinguished.¹ Aravalli basin in India is considered to be one of the most ancient phosphorite bearing basins. Phosphorites of Aravalli basin mainly are of a cyanobacterial nature and they are referred to as stromatolitic phosphorites. Their age is estimated as 1000-1500 million years, which is considered to be Middle Proterozoic.^{1,2} Later, it was suggested that Aravalli super group was of Early Proterozoic age (2.1 \pm 1.9 Ga). The age of Jhamarkotra site (phosphatic dolomites) of the Aravalli basin was determined to be 2.11 \pm 2.06 Ga.³ Phosphorites are still unknown in the Archaean Eon (2.5-3.8 Ga). Their absence is generally considered to be connected to the absence of an atmosphere enriched in oxygen.¹

Early Proterozoic (2.04 Ga) phosphorites were collected by V. Melezhik and A. Lepland in 2005. The period of 2500-2000 Ma is heralded by several hallmark events such as: the onset and decline of the greatest positive excursion of $\delta^{13}\text{C}_{\text{carb}}$ (Lomagundi-Jatuli Paradox); the development of a significant seawater sulphate reservoir; the abundant deposition of anomalously organic matter (OM)-rich sediments; the oldest known significant petroleum deposits (Shunga Event); and Melezhik *et al.*⁴ reported the appearance of first known marine phosphorites at 2000 Ma.

*astafieva@paleo.ru; +7 495 339-7911; fax +7 495 339-1266

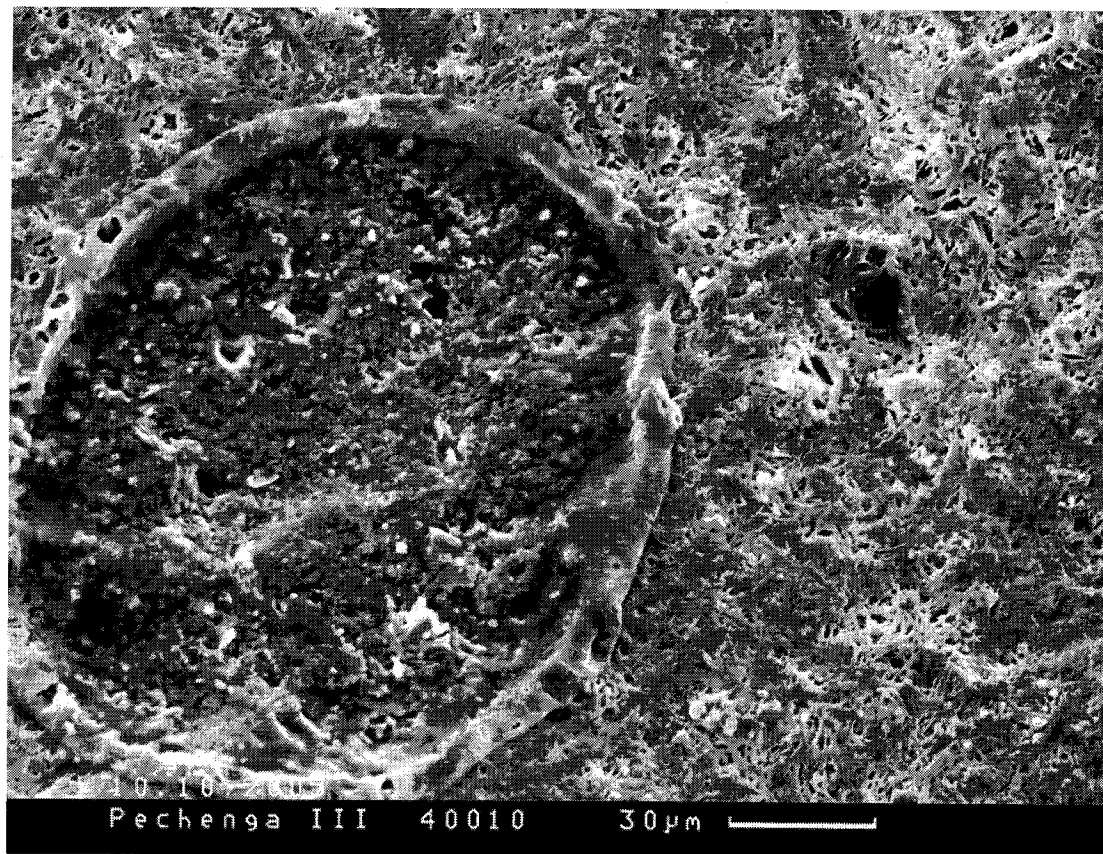
The phosphorites under discussion were discovered in the Pechenga Greenstone Belt. They occur as numerous rounded, soft-deformed, clasts in fine-pebble intra-formational conglomerates, forming two separate (c. 200 m-thick) turbidite fans within the 1000 m-thick OM- and sulphide-rich turbiditic greywackes of the Pilgajärvi Formation in the Pechenga Greenstone Belt, Kola Peninsula (NW Russia). Carbonate-fluorapatite is the main mineral in the phosphorite clasts. OM, framboidal and micronodular pyrite, as well as inclusions of quartz and chlorite, are additional components.⁴ Many clasts show microlayering with a variable degree of soft-deformation, implying that they were derived from non-lithified, bedded phosphorites.

The origin of phosphorites is well documented and ancient microfossils in phosphorites have been compared with microorganisms of recent cyanobacterial mats.⁵⁻¹⁵ The peculiarity of the study of recent phosphorites was that: 1) they were under investigation using Scanning Electron Microscopes with Microprobe analysis in considerable (mass) quantity; 2) all samples were treated with acids for 30-60 seconds, and then washed and dried. This was done in order to receive a surface relief of the samples that appears due to the great difference in the solubility of the carbonates, phosphates and siliceous components, as well as the organic-mineral complexes.

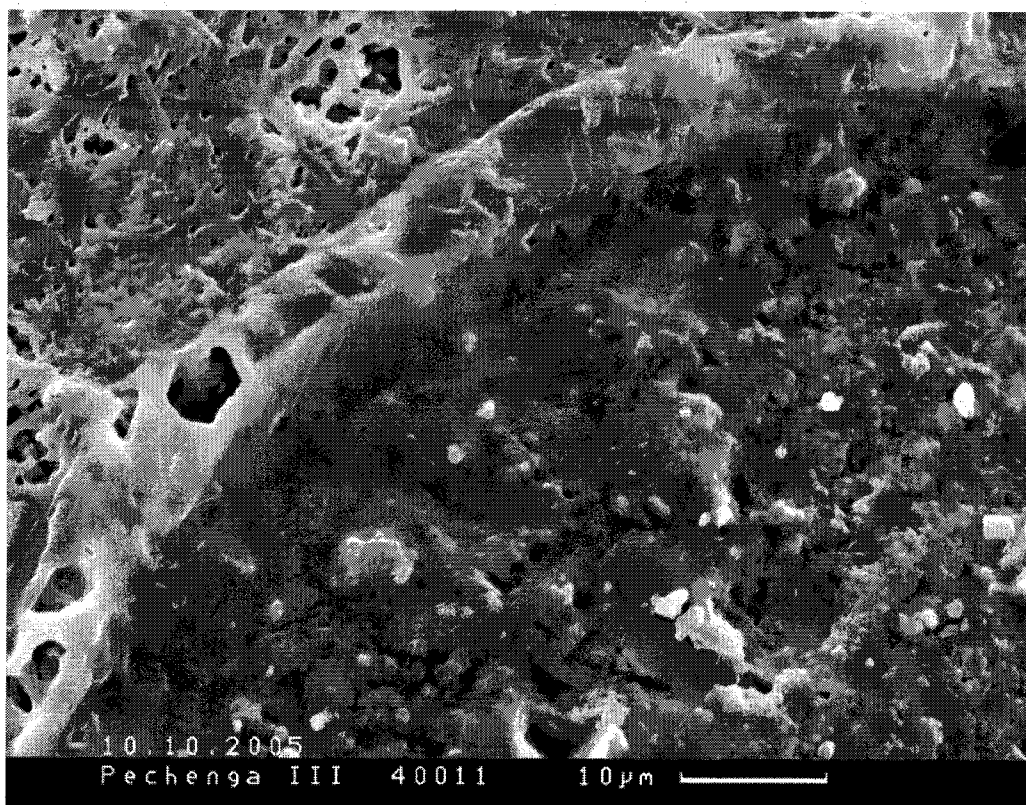
The phosphorite pebbles in the samples under investigation were found to contain numerous and diverse remains of fossil microorganisms.

They can be divided into three groups: 1) microorganisms of the same age as host rocks; 2) endoliths (i.e., forms that inhabited rocks that formed earlier); and, finally 3) subsequent contamination. This paper is devoted to structures of the first group which is comprised of fossil biomorphic structures that were organically interlaced within (and representative of) the host rocks. The biomorphic structures that were encountered exhibit rather diverse morphologies. There are filaments and thread, coccoidal, oval and rod-shaped forms, etc. and framboidal structures are also of interest.

1. Figure 1.a & b shows almost circular forms. It is rather difficult to judge their external form, but their diameter exceeds 100 μm .



a.



b.

Figure 1a. Ring-shaped, sack-shaped, or spherical biomorphic microstructure with b. detail of edge of ring-shaped biomorphic microstructure.

II. Their chemical composition differs slightly from that of the host rocks. Although sulfur is practically absent in the rock matrix (Fig. 1c), these well of these microstructures have sulfur content that is comparable to their phosphorus content (Fig. 1d). It is considered probable that their formation was connected with sulfur cycle, and is associated with the vital activity of sulfur bacteria or sulfate-reducing bacteria in particular. This conforms to supposed enrichment of marine waters by sulfates⁴ during the 2.0-2.5 Ga period. It is considered probable that we have some rather highly organized forms with complicated (complex) external structures which may represent a new genus.

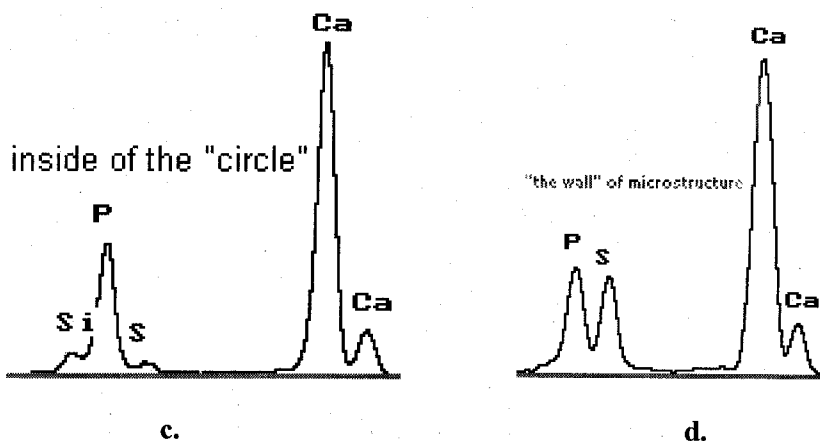
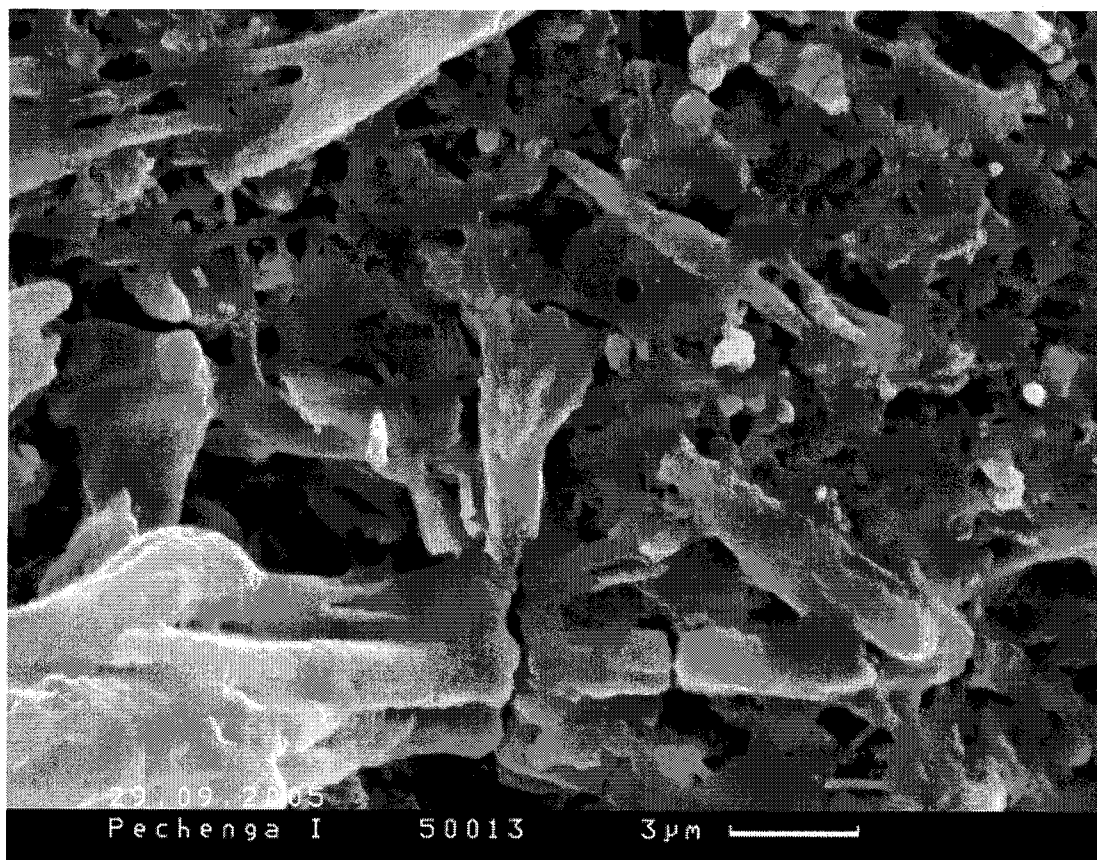
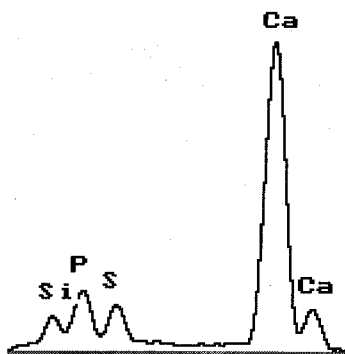


Figure 1c. Spectrum of interior rock inside spherical biomorphic structure and b. wall of the microstructures showing significant increase in sulfur content.

III. The diameters of the filament or thread-like forms are typically $\sim 1.0\text{--}1.5\mu\text{m}$, although they can be as large as $3\mu\text{m}$ (fig. 2a) and their length may exceed $20\mu\text{m}$. Sometimes it seems that they gathered in bunches, surrounded by sheath or external envelope.



a.



b

Figure 2.a. Scanning electron microscope image of filaments and b. the spectrum.

It is interesting that the forms shown in Fig. 2.a. have morphological characteristics of multiseriate trichomes such as are known in recent cyanobacteria of the genus *Microcoleus* that is common in modern halophilic mats and the fossil form *Siphonophycus*. (Note: Images of those forms are shown in Figs 2a, 3a, 4a, 16a of References 10, 13 and 15.)

Figure 3 shows images and the associated chemical composition for a mat-like network of interlacing filaments. The chemical composition of ancient, presumably bacterial, forms and host rocks (phosphorites) is identical, indicating that the bacterial fossilization occurred simultaneously with sedimentation.

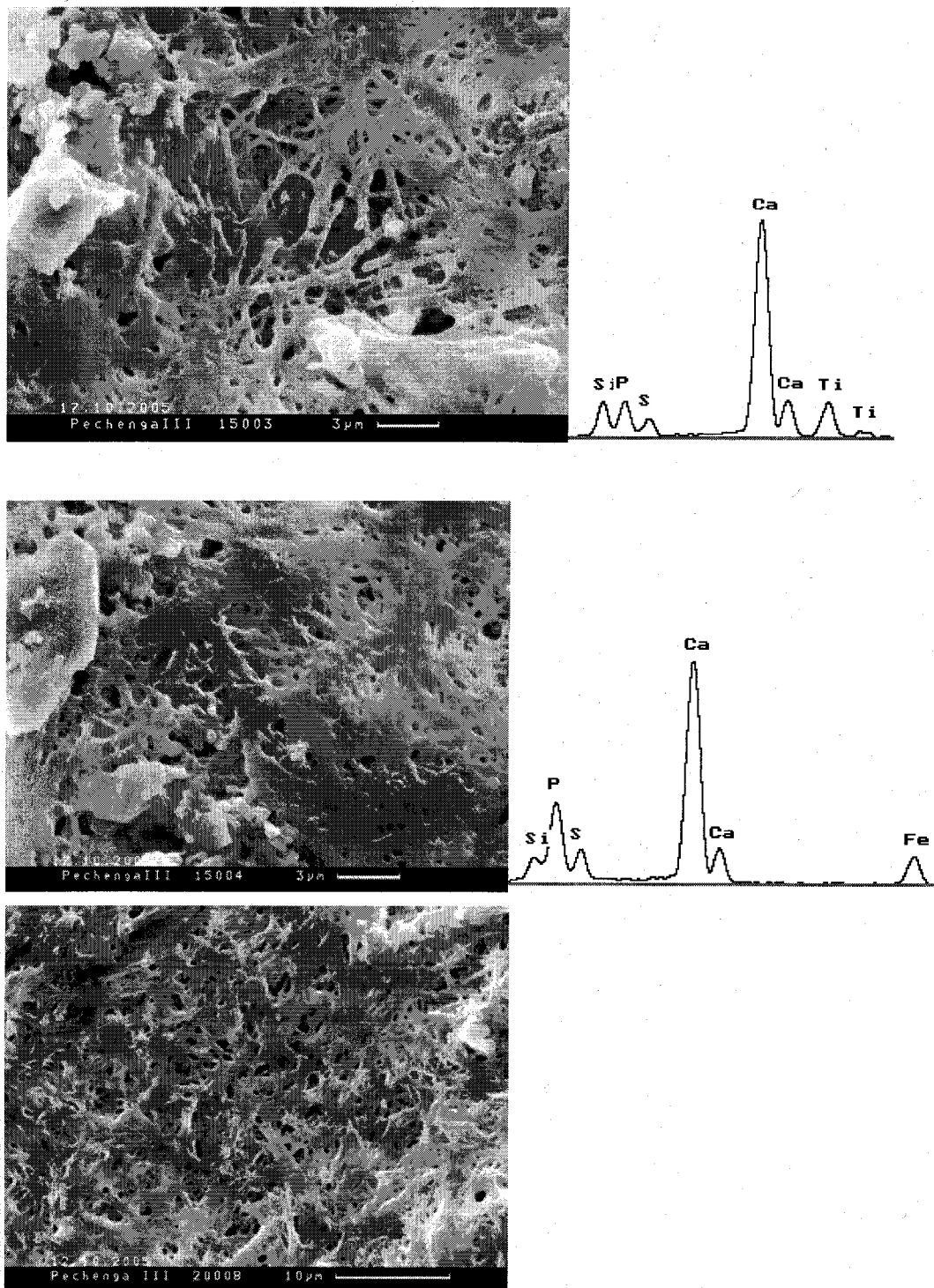


Fig. 3. Mat-like network of interlacing filament microstructures shown alongside their chemical compositions.

III. Elongated-oval or rod-shaped forms (Figure 4) could be comparable to polymorphic cells of recent cyanobacteria *Rhabdoderma* from alkaline mats or purple bacteria such as *Ectothiorhodospira* (See References 10; 13; 15, Fig. 6; 16, Fig.14-1). Attention should be paid to the resemblance with the picture of microorganisms from the upper layer of microbial mat of Bolsherechensk spring (North Baikalian region of Buryatia – Baikal rift zone), developing under the temperature about 54°C, pH 9.7 and sulfide content 2.8 mg/l (these characteristics correspond to alkaline hydrotherms). This layer is represented by oval cells of *Syneccoccus elongates* (representatives of this genus could be co-dominants under increased temperature) and by threads of *Chloroflexus aurantiacus* and *Phormidium* sp. The upper sub-zone of the layer is occupied by cyanobacteria *Syneccoccus elongates*, and in the deeper layer mats of *Phormidium* sp. predominate. Filamentous green bacteria *Chloroflexus aurantiacus* can be found all over the mat in an almost equal quantity [16, fig. 11a].

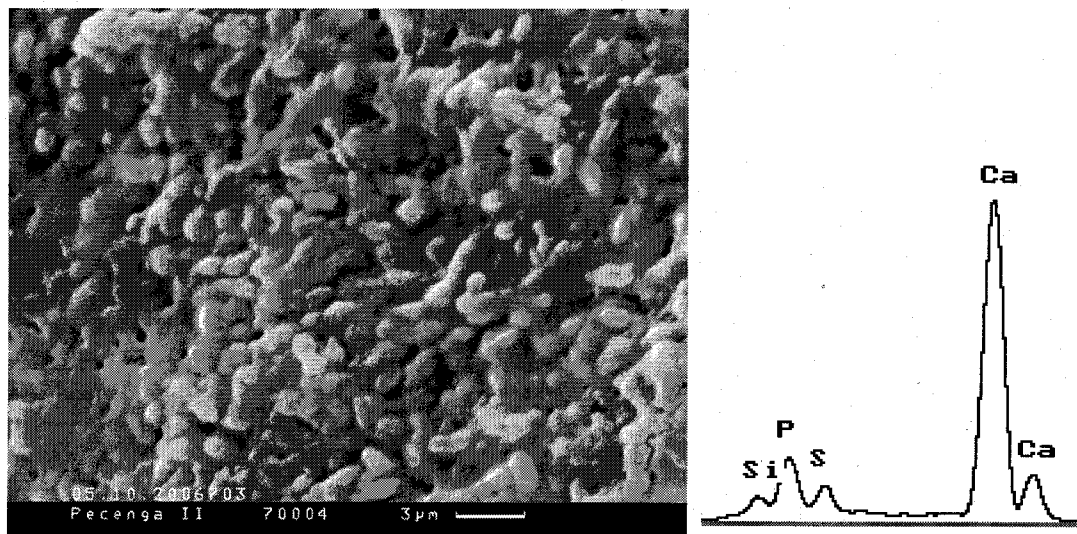


Figure 4. Rod-shaped, oval and filament microstructures and their spectrum.

IV. The size and morphology of the rounded, coccoidal forms with diameters of ~ 1.5 µm (Figure. 5) are similar to the purple bacteria *Thiocapsa* from recent halophilic mats [See Reference 10; 13; and 15, fig. 7a].

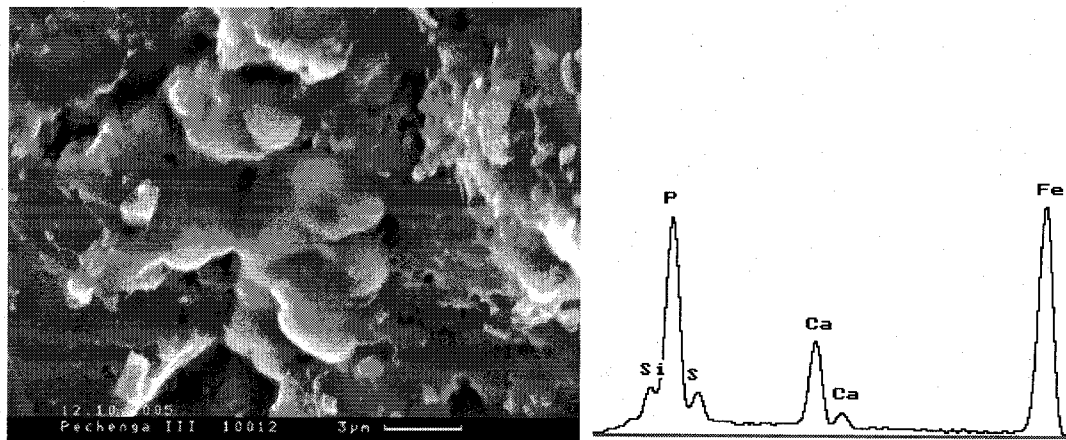


Figure 5. Coccoidal microstructures and their spectrum.

V. It is necessary to note the rare framboids (Fig. 6) that presumably consist of pyrite. The framboid diameter is about 15 µm. It has rounded form and consists of crystallites with smoothed angles. Framboids are widely spread in different types sedimentary rocks from many different ages. They are also found in modern marsh sediments, peat bogs, and in marine and oceanic silts. There is little doubt that framboids are shaped by the way that the crystallization of amorphous iron sulfides developed during the early stages of diagenesis in the local

centers of hydrogen sulphide contamination. The formation of framboidal structures is connected with bacterial processing followed by the mineralization of organic matter. At least, in marine conditions the precipitation of framboidal structures is connected with vital activity of sulfate reducing bacteria (SRB) [17 □ 22]. They can serve as mineral biomarkers providing indirect evidence of the vital activity of sulfate reducing bacteria during the formation of thin layers of the cyanobacterial mat components encountered in the rocks under investigation.

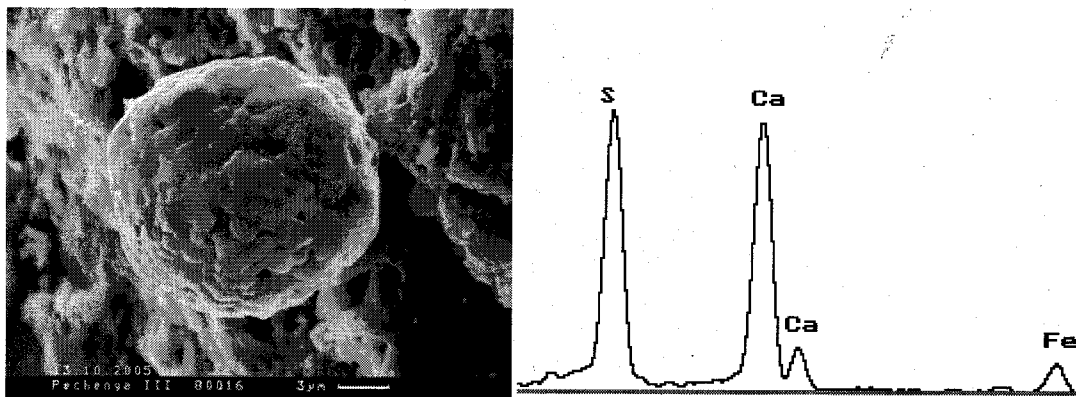


Figure 6. Framboidal(?) microstructure and its spectrum.

CONCLUSIONS

Thus it is probable that we have all of the components of a cyano-bacterial mat. It is known that cyano-bacterial mats represents prokaryotic benthic communities united in a physical structure by the slime (glycocalyx) as a forming tool which transforms the community into a morphologically unified unit. In these communities phototrophic bacteria dominate, and among them are the cyanobacteria are the main producers of organic matter. They are primarily responsible for the mat structure²⁰ As a rule, oscillatorilaeen cyanobacteria are the dominant forms representing motile filament organisms. In modern thermophilic mats there is the halophile and alkalophile - *Microcoleus chthonoplastes*, which forms multiseriate filaments with multiple trichomes within a common external envelope of sheath. Phototrophic bacteria (e.g., green *Cloroflexus aurantiacus*) in thermophilic mats, and purple bacteria (e.g., *Thiocapsa*, *Ectothiorhodospira*) in halophilic and alkalophilic mats provide anoxygenic photosynthesis under extreme conditions for cyanobacterial growth. Cyanobacteria may grow under favourable conditions by organotrophic growth by oxidizing products of vital functions of cyanobacteria or by oxidizing of hydrogen sulphide and, in such a way, they take part in sulphur cycle. These microorganisms occupy the middle regime. On one hand, they delay photosynthetic oxygen that is received from the cyanobacteria, and on the other hand, they protect the cyanobacteria from the hydrogen sulphide that is produced by the SRB in the lower layers of mat. It is considered quite possible that the formation of the above mentioned spherical forms with a high content of sulphur and calcium is connected with this process. Sulfide-genesis and methane-genesis are in concurrent dependence, the predominance of one or the other of these processes is determined by the sulfate content²³

It is considered logical to assume, that we are dealing with a cyano-bacterial mat, probably alkalophilic or halophilic. Moreover, the presence of framboidal iron sulphide suggests the presence of the sulfate-ion in the water basin or in the silt. This is confirmed by the presence of sulphur in practically in every chemical analysis carried out on these forms, because the layer of filamentous sulphur bacteria (which is typically situated under the layer of the oxygenic phototrophs) is connected the deposition of gypsum (CaSO_4).²⁰

If all of the components of the supposed mat were found separately and the laminated mat structure was not locked in, there is the possibility that all of the described components of a cyanobacterial mat could have developed independently. Representatives of *Rhabdoderma* are widely spread in the plankton and the planktonic mode of life is also possible for other cyanobacteria and the purple bacteria. For this reason, it is impossible to exclude that all these bacteria were planktonic and precipitated on the bottom only after extinction.

Thus, it is seen, that the Lower Proterozoic phosphorites, as well as younger: Cambrian Khubsugul, Early Cambrian and Sinian phosphorites of Yantzy Region of China and many other phosphorites have biogenic

origin, that is either bacterial or is connected with cyanobacterial mats.²⁴ There are no principle differences in nature of these phosphorites.

It is extremely important to underline that almost all known mineral compounds of phosphorus in the crust of the Earth are salts of orthophosphoric acid (H_3PO_4) and that the presence of oxygen is a necessary condition for formation of this acid.

Thus it is quite clear that the studied phosphorites were formed in the conditions of a warm shallow-water basin with oxygen-enriched waters.

ACKNOWLEDGMENTS

The authors are grateful to V. Melezhik and A. Lepland for vested material; L.M. Gerasimenko, T.N. German, G.T. Ushatinskaya, E.A. Zhegallo for valued advice during discussion of the material; A.V. Kravtsev and L.T. Protasevich for assistance with the CamScan-4 Scanning Electron Microscope.

The study was executed within the framework of the complex program of basic research of the Presidium of the Russian Academy of Sciences "Origin and Evolution of Biosphere" (subprogram II) and was supported by the Russian Foundation for Basic Research, projects 05-04-48008 and SS-974.2003.5.

REFERENCES

1. Yanshin A.L., Zharkov M.A., *Phosphorous and potassium*, Nauka, Novosibirsk, pp 1-189, 1986..
2. Yanshin A.L., [Evolution of geological processes and phosphorites of boundary layers of Precambrian-Cambrian of the Siberia] *Geology of phosphorite sites and problems of phosphoritogenesis*, izd-vo IG&G SO AN USSR, Novosibirsk, 13-14, 1982.
3. Purohit, R., Bekker, A., [Geochronologic and geochemical constraints on the age of the Jharmarkotra carbonates from the Aravalli supergroup, North-western India] *Geol. Soc. America Abstracts with Programs*, Vol. 36, No. 5, pp. 1-341, 2004.
4. Melezhik, V.A., Lepland, I., Rozanov, A.Yu., Astafieva M.M., [2000 Ma phosphorites in the context of evolution of Palaeoproterozoic ocean chemistry] *Abstr. II Int. Paleont. Congress*, June 17-21, 2006, Beijing, China, Univ. Sci. @ Techn. China Press, 45-46, 2006.
5. Lucas J., Prevot L., [Synthese de l'apatite par voie Bacterienne a partir, de matiere organique phosphatee et de divers carbonates de calcium dans des eaux douce et marine naturelles] *Chemical Geol.*, No 42, 101-118, 1984.
6. Rozanov A.Yu., Zhegallo E.A., [On the problem of genesis of ancient phosphorites of Asia] *Lithology and minerals*, No 3, 67-82, 1989.
7. Zhmur S.I., [Cyanobacterial benthic community is the main producer of the organic matter of marine biolithogenic rocks rich in carbon] *The problems of pre-anthropogenous evolution of the biosphere*, 294-303, Nauka, Moscow, 1993.
8. Zhmur S.I., Gorlenko V.M., Rozanov A.Yu., Zhegallo E.A., Lobzova R.V., [Cyanobacterial benthic system-producer of carbonaceous matter of shungites from the Lower Proterozoic of Karelia] *Lithology and minerals*, No 2, 122-124, 1993.
9. Briggs D.E.G., Kear A.J., Martill D.M., Wilby P.R., [Phosphatization of soft-tissue in experiments and fossils] *Journ. of the Geol. Soc. London.*, 150, 1035-1038, 1993.
10. Gerasimenko L.M., Goncharova I.V., Zavarzin G.A., Zhegallo E.A., Pochtareva I.V., Rozanov A.Yu., Ushatinskaya G.T., [Dynamics of deliverance and absorption of phosphorous by cyanobacteria] *Ecosystem reorganizations and evolution of biosphere*, Issue 1, 348-353, Nedra, Moscow, 1994.
11. Goncharova I.V., Gerasimenko L.M., Zavarzin G.A., Ushatinskaya G.T., [Formation of mineral phosphate microtubes in the presence of halophilic cyanobacterium *Microcoleus chthonoplastes*] *Current Microbiology*, 27, 187-190, 1993.
12. Zhmur S.I., Burzin M.B., Gorlenko V.M., [Cyanobacterial mats and formation of carbonaceous rocks of Precambrian] *Lithology and minerals*, No 2, 206-214, 1995.
13. Gerasimenko L.M., Goncharova I.V., Zhegallo E.A., Zavarzin G.A., Zaytseva L.V., Orleanskiy V.K., Rozanov A.Yu., Ushatinskaya G.T., [The process of mineralization (phosphatization) of filament cyanobacteria] *Lithology and minerals*, No 2, 208-214, 1996.

14. McKay D.S., Rozanov A.Yu., Hoover R.B., Westall F., [Phosphate biomineralization of Cambrian microorganisms] in *Instruments, Methods, and Missions for Astrobiology. Proc. SPIE*, 3441, 170-176, 1998.
15. Zhegallo E.A., Rozanov A.Yu., Ushatinskaya G.T., Hoover R.B., Gerasimenko L.M., Ragozina A.L. *Atlas of microorganisms from ancient phosphorites of Khubsugul (Mongolia)*, Huntsville, Alabama, USA, pp. 1-168, 2000.
16. Namsaraev Z.V., Gorlenko V.M., Namsaraev B.B., Barkhutova D.D., *Microbial communities of alkaline hydrotherms*, SB RAS, Novosibirsk, 11, 2006.
17. Kohn M.J., Riciputi L.R., Orange D.L., [Sulfur isotope variability in biogenic pyrite: reflections of heterogeneous bacterial colonization?] *Amer. Mineralogist*, 83, 1454-1468, 1998.
18. Taylor G.R., [A mechanism for framboid formation - the role of bacteria. A reply to Dr. S. I. Kalogeropoulos and a further contribution] *Miner. Deposita*, 18, 129-130, 1983.
19. Gerasimenko L.M., Zavarzin G.A., [Relict cyanobacterial communities] *The problems of pre-anthropogenous evolution of the biosphere*, Nauka, Moscow, 222-253, 1993.
20. Zavarzin G.A., Kolotilova N.N., *Introduction into environmental microbiology*, 256 p., Knizhniy dom «University», Moscow, 2001.
21. Astafieva M.M., [Framboidal Structures of Black Shales from Cambrian of the Siberian Platform and Permian of the Barents Sea Shelf] *Paleont. Journ.*, 1, 3-8, 2005.
22. Astafieva M.M., Rozanov A.Yu., Hoover R., [Framoids: their structure and origin] *Paleontol. Journ.*, 39, pp. 457-464, 2005.
23. Gerasimenko L.M., Ushatinskaya G.T., [Phosphatization] *Bacterial Paleontology*, pp. 59-65, PIN RAS, Moscow, 2002.
24. Shkolnik E.L., Tang Tianfu, Eganov E.A., Rozanov A.Yu., Baturin G.N., Zhegallo E.A., Xue Yaosong, Yu Conliu, C. Jehl., Piper D., Medrano P.M., *Nature of Phosphate grains and phosphorites of the largest basins of the world*, pp. 1-206, Dalnauka, Vladivostok, 1999.